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SELENIUM: A TRACE ELEMENT FOR HUMAN AND VEGETABLES

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ABSTRACT - Selenium (Se) is an essential micronutrient for the growth, development and metabolism of animals, including humans. It is an integral part of a set of proteins, the selenoproteins, with antioxidant action, involved in the metabolism of thyroid hormones, growth regulation, cell viability, immune system functions and reproduction. This element fulfils the same function in vegetables, although it does not play an essential role in their nutrition, so it is currently included in the group of beneficial elements. It is introduced into the food chain by ingesting plants and products derived from them. Plants assimilate Se compounds, present in the soil, mainly in the form of inorganic compounds of selenate (Se^{6+}) and selenite (Se^{4+}). Both have water solubility and are part of the metabolic processes that occur in humans. In view of the above, the objectives of this literature review were to present information on some of the main aspects of selenium for humans and plants, describing its forms of absorption, benefits, problems related to its deficiency and its use in food biofortification. Selenium (Se) has several benefits for plants and human health, and for humans, when administered in ideal concentrations. In addition to providing a healthy diet, it can act as an antioxidant, playing an important role in protecting against viral infections.
Keywords: Biofortification, human health, selenate, selenite, COVID-19.

SELÊNIO: OLIGOELEMENTO PARA HUMANOS E VEGETAIS

RESUMO - O selênio (Se) é um micronutriente essencial para o crescimento, desenvolvimento e metabolismo dos animais, incluindo o ser humano. É parte integrante de um conjunto de proteínas, as selenoproteínas, com ação antioxidante, envolvidas no metabolismo dos hormônios da tireóide, na regulação do crescimento, na viabilidade celular, nas funções do sistema imune e na reprodução. Esse elemento cumpre a mesma função em vegetais, embora não tenha papel essencial na sua nutrição, por isso está atualmente incluído no grupo de elementos benéficos. É introduzido na cadeia alimentar por ingestão de plantas e de produtos que delas derivam. As plantas assimilam os compostos de Se, presentes no solo, principalmente, na forma de compostos inorgânicos de selenato (Se^{6+}) e selenito (Se^{4+}). Ambos apresentam solubilidade em água e fazem parte dos processos metabólicos que ocorrem em humanos. Em face ao exposto, os objetivos desta revisão de literatura foram apresentar informações sobre alguns dos principais aspectos do selênio para os seres humanos e vegetais, descrevendo suas formas de absorção, benefícios, problemas relacionados à sua deficiência e seu uso na biofortificação de alimentos. O selênio (Se) apresenta diversos benefícios para os vegetais e para a saúde humana, sendo que para os humanos, quando ministrado em concentrações ideais, além de proporcionar uma dieta saudável, pode atuar como antioxidante, desempenhando papel importante na proteção a infecções virais.
Palavras-chave: Biofortificação, saúde humana, selenato, selenito, COVID-19.

INTRODUCTION

Trace elements are inorganic elements present in small amounts in living organisms. According to the World Health Organization (WHO), these elements are classified into three groups: essential elements, non-essential elements and toxic elements. Such classification is based on the properties they possess, as well as their importance in relation to human beings (WHO, 1987; FAO, 2001).

Selenium (Se) is one of those trace elements which are essential for human and animal health. It is considered essential for the synthesis of the amino acid selenocysteine, which is involved in the formation of 25 proteins essential for mammalian metabolism. Thus, with the increase in global interest in its features, scientific research related to its use has expanded. In general, ideal concentrations of Se in the body have been related to the proper functioning of animal somatic cells, due to their antioxidant properties, contributing to the delay of aging. Furthermore, the presence of Se also helps in the treatment of cardiovascular diseases and neoplasms, muscular dystrophy, multiple sclerosis, osteoporosis, reproducibility and muscular disorder (SCHWARZ; FOLTZ, 1957; HIMOTO et al., 2011).

Despite the benefits, dietary supplementation with Se should be well planned. This is because the limit between the required levels and those which are considered toxic to animals is very close (OLIVER; GREGORY, 2015). In plants, Se helps to combat oxidative stress, caused by oxygen free radicals; however, when

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supplied in high concentrations, it can also trigger toxicity (TURAKAINEN et al., 2005). Se can be found in soil, mainly as selenate and selenite, presenting chemical properties similar to those of sulfur (S) (WHANGER, 2002; MARTINEZ et al., 2009). Furthermore, the levels of Se in plants, animals and humans are directly related to its concentration in the soil, which in turn is associated with its pedology, genesis and location in crop and pasture areas (ANDERSON et al., 1961).

In Brazil, there are still few studies carried out with the objective of introducing Se in foods. As such, it is essential to develop specific studies in an attempt to define strategies, dosages, forms of application, as well as the definition of limit amounts to be ingested for their proper use (FERREIRA et al., 2002). Today, it is already known that insufficient intake of Se, as well as other mineral elements such as iron (Fe), zinc (Zn), iodine (I) and vitamins A and B-12, can cause the so-called 'Hidden Hunger', that is, a non-explicit nutritional deficiency, which occurs silently and can cause disorders in the immune system, in addition to diseases such as anemia and reduced work capacity (MILLER; WELCH, 2013; LOUREIRO et al., 2018).

Based on the above, this review concentrates information on the main aspects related to the mineral element selenium (Se), both for humans and for plants, describing its forms of absorption, benefits, problems related to deficiency, as well as aspects related to it. its use in food biofortification.

DEVELOPMENT

Selenium History

Selenium (Se) was discovered in 1817 by the Swedish drugstore Jons Jakob Berzelius (TERRY et al., 2000), being classified as a metalloid element belonging to Group 16 (VI A) of the Periodic Table (RIZZO et al., 2007). However, it became a known element, but with no known physiological utility. It was around the year 1928 that Dr.Kurt Franke, studying plants and grains, discovered that She was an etiological agent of toxic effects (FARINA, 2000).

In 1957, Klaus Schwarz, based on some results of experiments, started to defend the essentiality of Se in the diet. This is because, this researcher verified that the presence of Se, in the diet of a group of rats, contributed to preventing the so-called hepatic necrosis in these individuals. Subsequently, a similar effect was observed in other pathological disorders identified in sheep, cattle, pigs and poultry (HARTLEY et al., 1961; CALVERT et al., 1962).

Research on Se and its interaction with humans, plants, soils, and fertilizers has also been expanding since the 1950s, focusing mainly on the study of its relationship with humans. However, the scientific literature on this mineral only began to increase significantly from the 1990s onwards. This is because it was in this period that great advances were made in the development of sensitive techniques for the determination and quantification of mineral elements in various components such as human tissues, plants, soils and fertilizers. According to several of these studies, human absorption of Se is influenced by its content in food, which is directly associated with its availability in the environment, especially in soil (PIETINEN et al., 2010; RAYMAN, 2012; MEHDI et al., 2013).

Effects of Selenium on Humans

Oilseed foods, such as Brazil nuts (*Bertholletia excelsa*), are the main sources of selenium (Se) for human consumption. Other foods that contain Se are beans (*Phaseolus vulgaris*), especially black and red beans, as well as cereals, whole wheat flour and cornmeal, and meat, especially beef and chicken liver. In fish, concentrations are very high, as in canned sardines and tuna. Eggs and milk, which are foods consumed almost daily, also have Se in their compositions (FERREIRA et al., 2002).

Se is among the important elements of the immune system. In general, it is involved in the antioxidant response, where it plays an essential protective role (SANTIAGO; SOUZA, 2020) against viral infections such as, for example, SARS, SARS-CoV-2, H5N1 and H1N1 influenzas, Ebola hemorrhagic fevers and HIV/AIDS (FAIRWEATHER-TAIT et al., 2011; DAVIS et al., 2012; CARDOSO et al, 2015; SANTIAGO; SOUZA, 2020). In these, Se acts by reducing the inflammatory process, which, consequently, reduces its metabolism, leading to a probable metabolic deficit after this activity (HELLER et al., 2021). According to Fakhrolmobasheri et al. (2021), Se deficiency can be considered an indicator of the severity, mortality and global risk of COVID-19 and other viral conditions.

Following the same line of studies, researchers have shown the association between levels of Se, in the body of patients, in relation to the clinical course of COVID-19. In one of these studies, Majeed et al. (2021) verified Se concentrations in healthy adult subjects and COVID-19 patients. According to the researchers, it was observed that the content of this mineral element was lower in those individuals who had the disease (43.3%) when compared to the control group (20%), giving average values of 69.3 ± 8.8 ng mL^{-1} and 79.1 ± 10.9 ng mL^{-1}, respectively. Similar results were observed by Wang et al. (2021). According to the researchers, the decrease in the severity of the disease and the risk of mortality, may be directly associated with the lower availability of Se in the body after COVID-19. Thus, higher levels of Se in the body may indicate a greater chance of survival in the face of infection by the disease, where rapid supplementation of this mineral, combined with other elements, can be considered an adjuvant therapeutic measure (HELLER et al., 2021).

In addition, other published studies also indicate that low Se concentrations (less than 45 μg L^{-1}) are associated with deaths from cardiovascular disease and stroke (VIRTAMO et al., 1985). This finding strengthens the idea that Se can also play a key role minimising the development of chronic diseases, reducing inflammatory activity and benefiting the antioxidant defence system (WALSTON et al., 2006).

In this sense, the daily supplementation of Se in humans, and also in animals, has been suggested by the scientific community. The Institute of Medicine of the US National Academy recommends an intake of 55 µg day^{-1} for adults, with the maximum tolerable intake for this group being 400 µg day^{-1} (BENDICH, 2001). However, these reference values may vary by country. In Germany, for example, between 60 and 120 µg L^{-1} day^{-1} is recommended for women and 79 to 130 µg L^{-1} day^{-1} for men (WILHELM et al., 2004). In Brazil, 34 µg day^{-1} is recommended for adults and between 6 and 21 µg day^{-1} for children aged 0-10 years (BRASIL, 2005).

Despite that, attention should be paid to high levels of Se in the body, as this element can also cause chronic toxic effects to individuals, causing selenosis that, in the acute phase, can cause nervous system disorders, irritability, diarrhea, fatigue, nausea and rash (MANGIAPANE et al., 2014). Animals that ingested plants of the genus Astragalus, classified as accumulators of Se, showed symptoms of two types of selenoses: alkaline disease and false stagger, both irreversible to the animals, leading them to death (FRANKE, 1934).

Selenium in Soil

Selenium (Se) occurs in different oxidation states: selenate (Se^{6+}), selenite (Se^{4+}), elemental selenium (Se^0) and selenide (Se^{2-}). In the oxidized forms, selenate and selenite are highly soluble in water, while in its elementary form it is practically insoluble (RIZZO et al., 2007). Thus, the bioavailability of Se does not only depend on its total concentration, but also varies, according to its predominant form in the soil (MARTENS; SUAREZ, 1997; LI et al., 2010).

The presence of Se in the soil solution is important for plants, as its content is directly related to its availability in the environment it grows. However, its content in soils is very low, ranging from 90 to 100 ppm (KABATA-PENDIAS, 2011). This bioavailability of Se for plants is governed by factors linked to the soil, such as clay and organic matter content and the most important factors controlling the forms of Se in the soil are pH and redox potential (EL-RAMADY et al., 2014).

Despite being a relatively scarce element in nature, Se is present in the soil (DHILLON; DHILLON, 2003). According to Prauchner (2014), the distribution of this mineral on the earth's surface is uneven, which results in rich/excessive geo-ecosystems and others deficient in the micronutrient. In general, in arable soils around the world, its average content is 0.4 mg kg^{-1} (SAHA et al., 2017). However, in Brazilian soils its concentration is very low, being considered poor in this element (SILVA JÚNIOR et al., 2017; MIRLEAN et al., 2018).

Although the geographic distribution of Se varies greatly under natural soil conditions, selenate and selenite are the main inorganic selenium compounds to be formed (RYAN; DITRICK, 2000). Selenate predominates in alkaline soils and has greater mobility than selenite, which is normally found in neutral or acidic soils (KABATA-PENDIAS, 2011). Selenate is less sorbed than selenite, so the latter form is strongly adsorbed to solids such as Fe/Al oxyhydroxides, thus having low mobility in soils (LOPES et al., 2017). The difference in the adsorption behavior of selenate and selenite reflects the different bioavailability for plants, being the former the most available.

In selenate, binding is not limited to the complex in the outer sphere, the predominant adsorption mechanism, but there are also contributions from complexes in the inner sphere, which gives a mixture of surface complexes between the outer and inner spheres (JORDAN et al., 2013). Selenite is bound by ligand exchange, forming internal complexes that are not reversible (MCBRIDE, 1994).

In Brazil, according to Lessa et al. (2016), the effect of soil preparation on selenate adsorption can be attributed to the presence of anions such as sulfate and phosphate. These anions are more abundant in cultivated soils than in uncultivated soils, which suggests that uncultivated soils adsorb much more compared to cultivated ones. According to Fordyce (2007), the higher Se content in cultivated soils may be related to the application of phosphate fertilizers, which can contribute to the partial saturation of positive charge sites. These sites are occupied, especially, with phosphates and sulfates, making these soils reached a lower maximum capacity of adsorption of Se.

Despite the above, there are few studies that have investigated Se sorption in Brazilian soils (MOUTA et al., 2008; GABOS et al., 2014). In most of them, sorption was investigated based only on the availability of high concentrations in the solution, and further studies are needed to help elucidate the processes of sorption and desorption of that mineral.

Due to its importance, Jones et al. (2017) used 33,241 data points to model recent (1980-1999) global distributions of Se in soil (Figure 1A). Using moderate climate change scenarios for 2080–2099 (Figure 1B), these researchers predicted that changes in climate and soil organic carbon content could lead to an overall decrease in concentrations of this mineral, particularly in agricultural areas. Therefore, these scenarios could increase the prevalence of Se deficiency in the world and, consequently, in food.

Selenium in Plants

Selenium (Se) can be found in organic and inorganic form in the atmosphere, soils, biomass, marine systems (WINKEL et al., 2015) and in the food chain, through plants (DHILLON; DHILLON, 2003). However, despite being an essential element for humans and animals, there is still no evidence about its essentiality for plants (TERRY et al., 2000). Despite this, there are studies that demonstrate its benefits for plants. Such benefits can range from participation in compounds and reactions in plant metabolism, even enabling increased productivity of some cultures, mainly due to the increase in antioxidant activity of some cells (GUPTA; GUPTA, 2017; SCHIAVON;

PILON-SMITS, 2017; ZHU et al., 2017). It is important to note that, in high concentrations, this element can cause cell oxidation, causing phytotoxicity and, thus, compromising plant development (LYONS et al., 2009).

Of the four inorganic forms of selenium available in soils, elemental selenium (Se^0), selenide (Se^{2-}), selenate (Se^{6+}) and selenite (Se^{4+}), the last two are the most absorbed by plants and predominant in the rhizosphere in soils cultivated (Figure 2). There is a great similarity in the chemical and ionic forms of Se with the forms of sulfur (S) and phosphorus (P), so that plants, for the absorption of selenate (Se^{6+}), use sulfate transporters (SO_4^{2-}) and, for selenite (Se^{4+}), they use phosphate transporters (PO_4^{3-}) (PEÑALOZA, 2017).

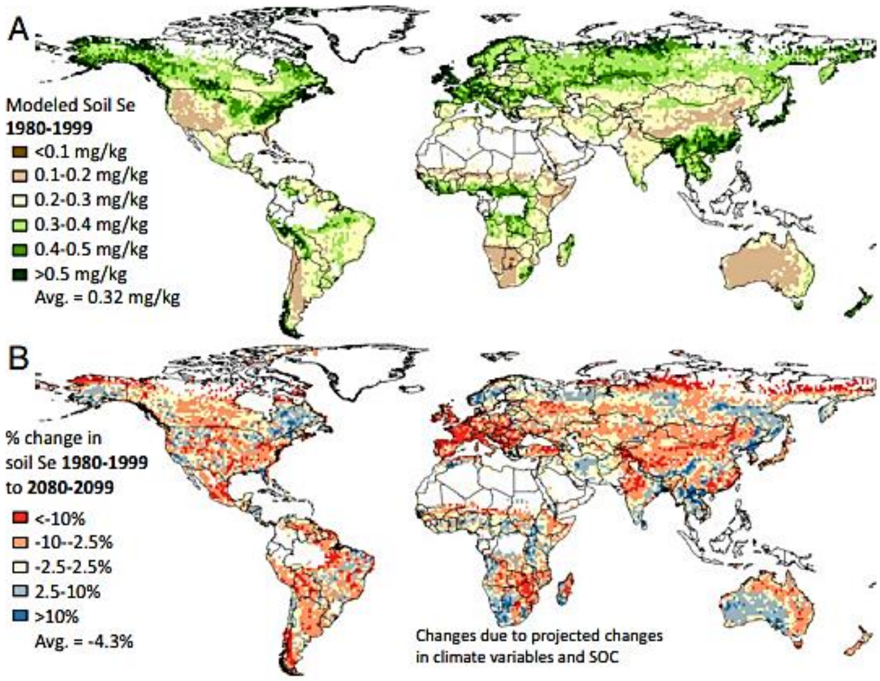

FIGURE 1 - Forecast of change in soil selenium concentration between 1980-1990 and 2080-2099. Adapted from Jones et al. (2017). PNAS = Proceedings of the National Academy of Sciences of the United States of America.

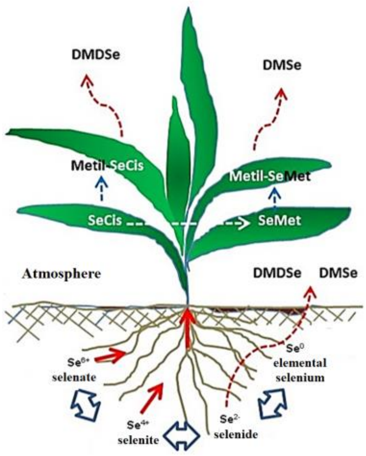

FIGURE 2 - Soil-plant-atmosphere interface and forms of selenium (Se). Adapted from: Winkel et al. (2015) and Gupta and Gupta, 2017.

Within the plant, Se is assimilated into tissues, through S metabolic pathways, in organic forms. Assimilation (Figure 2) basically consists of two reductions of Se, starting with the reduction of selenate (Se^{6+}) to selenite (Se^{4+}) and from this to selenide (Se^{2-}). Selenide is the form that is incorporated into cysteine, an amino acid (AA), which replaces the sulfur molecule (S) giving rise to selenocysteine (SeCis), and the synthesis of selenomethionine (SeMet) occurs from SeCis (Figure 3).

The AA SeCis and SeMet, incorporated into proteins, give rise to selenoproteins. SeCis and SeMet can also have a methyl group ($-CH_3$) added to their composition, forming methyl-SeCis (MeSeCis) and methyl-SeMet (MeSeMet). These two forms constitute more than 80% of Se in plants. In addition, they are also known as important precursors of dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe), being less toxic and volatile chemical species than SeMet and SeCis (PEÑALOZA, 2017).

Plants differ according to their ability to tolerate and concentrate selenium in their tissues, being classified into three groups: accumulating, non-accumulating and hyperaccumulating plants (ELLIS; SALT, 2003; HAWRYLAK-NOWAK, 2013). These differences are mainly related to the mechanisms of Se uptake and metabolism in each plant category (PRAUCHNER, 2014).

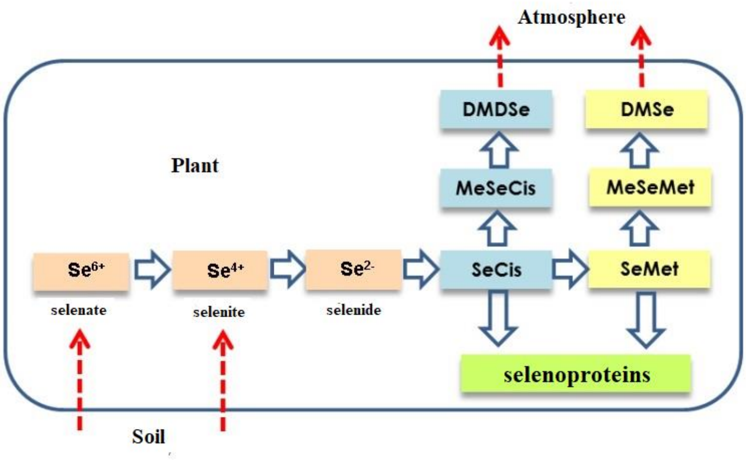

FIGURE 3 - Schematic diagram of selenium (Se) assimilation and metabolism in the plant. Adapted from: Winkel et al. (2015) and Gupta and Gupta (2017).

Accumulating plants, such as some species of the Asteraceae (FREEMAN et al., 2010), Brassicaceae (YUAN et al., 2013) and Fabaceae (WHITE, 2016), have the capacity to accumulate, in their dry matter, between 50 to 1,000 mg kg^{-1} of Se, without suffering any damage or compromising the integrity of the plant. Hyperaccumulator species, which can accumulate up to 15,000 mg kg^{-1} in their dry matter when grown under natural conditions, can be used as phytoremediators to remove excess Se from the environment (SAHA et al., 2017). Among the hyperaccumulators, some plant genera stand out, such as: *Stanleya*, *Astragalus*, *Neptunia* and *Xylorhiza* (BODNAR et al., 2012).

Most plant species of agricultural interest contain less than 25 mg kg^{-1} of Se in their dry matter and are considered non-accumulating (MARTINEZ et al., 2009; BODNAR et al., 2012; WINKEL, et al., 2015), being intolerant to high concentrations and excess in plant tissues, and may present symptoms such as: chlorosis, growth retardation, leaf wilting and plant death (WHITE, 2016).

Biofortification of vegetables with selenium

Selenium (Se) is essential in human nutrition. However, in several countries, including Brazil, the intake of Se per person is below what is considered ideal. The main justification is given by its low bioavailability and concentration in soils (VALLE et al., 2007). Knowledge of the factors that influence the absorption, translocation and accumulation of Se in plants can be a tool that will allow its increase in these organisms (NATASHA et al., 2018).

In Brazil, the Ministry of Agriculture, Livestock and Food Supply has included Se as a possible element to be added to fertilizers to increase it in the Brazilian diet, according to the Normative Instruction nº 46 (BRASIL, 2016). In addition, some actions have been taken to increase the intake of this mineral by humans, such as the use of food supplements or the biofortification of vegetables (PIETINE et al., 2010).

There are three main approaches to biofortification: agronomic, conventional plant breeding, and plant breeding using genetic engineering (SCHIAVON; PILON-SMITH, 2017; GARG et al., 2018). Among these three, agronomic biofortification, which aims to provide micronutrients that can be absorbed directly by the plant, through the application of mineral and/or foliar fertilizers and/or the improvement of solubilization and mobilization of mineral elements in the soil, is recognized as the simplest approach used to increase the levels of microelements in cultures (PILON-SMITS, 2010; FAIRWEATHER-TAIT et al., 2011; ÁVILA et al., 2013). This form of biofortification is also recognized as the most economically viable way to reduce mineral deficiency in the human diet (SZEREMENT et al., 2022). In Finland, some studies have shown that the increase in Se content in foods, by adding this mineral to fertilizers, is closely related to the decrease in health problems (ALFTHAN et al., 2015).

Genetics, another form of biofortification, may involve traditional and/or molecular strategies for plant breeding. In this type of biofortification, strains are selected taking into account the affinity of the transporters, giving preference to those with higher affinity for selenium (Se) in detriment to sulfur (S). Selection can also be performed based on the greater ability of some strains to accumulate Se-containing compounds in leaves and vegetative tissues to later translocate to grains or other edible parts (PRAUCHNER, 2014).

One of the first attempts in genetic engineering to improve the efficiency of Se phytoremediation was to manipulate the initial step of its metabolism, that is, the reduction of selenate. For this, it was performed the overexpression of ATP sulfurylase (APS1) in brown mustard (*Brassica juncea*). As a result, overexpression of APS1 led to increased reduction of selenate in the plant, resulting in a two- to three-fold increase in Se accumulation in shoots and roots (PILON-SMITS et al., 2009; ZHU et al., 2017; SARWAR, et al, 2020).

Another biofortification tool that can be used to increase Se content in plants involves the use of interactions between the culture of interest and microorganisms, such as selenorrhizobacteria, since microorganisms play an important role in the transformations and availability of Se (PATEL et al., 2018). Also, the combination of the use of plant growth-promoting bacteria (BPCP), which can contribute to stimulating the growth of their host (PATEL et al., 2018), when combined with agronomic applications of Se, can provide increased absorption and accumulation. of this mineral in edible parts of plants (SARWAR, et al., 2020).

In general, researchers have observed a positive effect of selenium supplementation for plant cultivation. For example, Mezeyová et al. (2022) found that biofortification with an aqueous solution of sodium selenate increased the selenium content of plant species, as well as affected the yield and content of other physiologically active components, including chlorophylls and certain minerals. Similarly, Puccinelli et al. (2019) observed a higher germination index and higher antioxidant capacity of sweet basil (*Ocimum basilicum*) grown hydroponically and supplemented with 4 or 8 mg L^{-1} of selenium. Pannico et al. (2020), studying the effect of sodium selenate applications on the bioactive compounds and mineral content of different vegetables, also found an increase in Se content in response to increasing doses applied.

Based on the above, considering that the response to this mineral is dependent on the dose and genotype used, studies should be carried out with a focus on clarifying the interaction between the genotype and the dose to be applied, in order to identify the combination that guarantees an ideal balance between yield and biofortification of the target species/genotypes. The potential success of food biofortification is based on the correct selection of target crops and the optimization and standardization of cropping systems. These are the prerequisites that guarantee sustainability in the production of foods enriched with micronutrients – because they are safe for consumption, present high quality, meet the recommended dietary intake standards for the target element, and are easy to introduce into diets in different regions of the world (PANNICO et al., 2020).

CONCLUSIONS

Although research on selenium (Se) has increased in number in recent decades, the complex interaction between this mineral and factors such as soil, water, atmosphere, and living beings, ends up requiring increasingly detailed research that does not only assess dosages and its effects, but also provide contributions to the elucidation of the processes that compose its chemical reactions in the different environments and organisms which it passes through.

Studies have shown that Se has several benefits for human and animal health, in which, related to the definition of its concentrations, it provides a healthy diet and, consequently, has increased people's interest in its supplementation. From this perspective, research should be continued so that the line that separates Se from benefit to toxicity in living organisms becomes increasingly clear, thus increasing safety in its use.

Thanks to techniques that combine agronomic biofortification, plant breeding, genetic engineering, and fertilizer management, the population of countries, such as Brazil, with soils poor in Se, have the possibility of having access to this essential micronutrient, through the consumption of staple foods that will be produced in an environment enriched with this mineral. Such a condition can promote the reduction of health problems resulting from the lack of Se in the diet.

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